PROJECT NUMBER : 2500
PROJECT TITLE : Fundamental Chemistry
PROJECT LEADER : J. I. Seeman
PREPARED BY : J. A. Fournier
PERIOD COVERED : December, 1990

I. INORGANICS AS NOVEL TOBACCO MATERIALS ADDITIVES

(Fournier, Kallianos, Paine, Podraza, Secor, Seeman)

A. **Objective:** To develop inorganic materials for novel applications for reduced sidestream, for burn-rate modification, and enhanced subjectives in cigarettes and for required properties in novel smoking materials.

B. **Results and Plans:** RSA Corporation's laboratory evaluation of the preparation of magnesite via a hydrothermal reaction of $Mg(OH)_2$ with CO_2 has been completed. Samples, all reported to be greater than 95% conversion, have been received and are in the process of being evaluated.

Subjective results on two cigarettes, one containing a paper filler of "recrystallized" $Mg(OH)_2$ and the other containing Reheis $Mg(OH)_2$ powder, were received. Both cigarettes which, gave 80% sidestream smoke visibility reduction with static burn times of approximately eleven minutes, exhibited positive subjectives. Microscopy results to determine the morphology of the two samples are pending and requests have been made for additional papers and cigarettes.

Smoking data on two sets of cigarettes prepared with papers containing mechanical mixtures at 92% to 8% and 78% to 22% of Baymag C magnesite and freshly prepared MgO, respectively, were received. Sidestream reductions of 52% for the paper containing a higher percentage of Baymag C magnesite and 67% for the paper containing a higher percentage of MgO with static burn times of 8.4 minutes and 7.6 minutes, respectively, were exhibited. It was originally hoped that the addition of MgO to magnesite would help improved ash integrity, however, this was not observed. Subjective evaluations are pending.

To support patent application PM-1511, requests for additional handsheets containing magnesite, $Mg(OH)_2$, and mixtures thereof have been made.

The kinetics of the dissolution of eitelite in water was investigated. The rate of solution of sodium decreased significantly with time, as the concentration of sodium in the solution increased. The rate of hydrolysis was found to be significantly slower in dilute sodium carbonate (1% total sodium). Thus it appears that low values of sodium can significantly retard the decomposition of eitelite, and improve the chances for papermaking.

The reaction between calcium hydroxide (portlandite) and magnesium bicarbonate was repeated at the same four ratios as conducted previously, so as to isolate the product as a slurry. Several of the previous preparations had proved difficult to resuspend in water after drying. X-ray results for the earlier set of reaction products

show calcium carbonate to be present as both calcite and aragonite. At low ratios of portlandite to magnesium, the magnesium phases are nesquehonite and/or hydromagnesite. At high ratios, the magnesium phases are hydromagnesite and/or brucite. Residual portlandite was also detected, probably occluded in the larger particles. In the latest preparations, now submitted for analysis, and awaiting results, coarse particles were removed by decantation.

Smoking results have been completed for three sets of cigarettes prepared with papers containing 20% MM $CaCO_3$ and 5 to 10% (depending on retention) aqueous "sol-gel" derived hydromagnesite/magnesium hydroxide mixtures with ratios of 50:50, 60:40, and 70:30, respectively. Sidestream reductions of 41% to 52% with static burn times of 7 to 8 minutes were observed with these models. The subjectives of the latter model were judged to be acceptable, exhibiting no negative attributes.

The use of calcium carbonate as a co-filler in "mag carbonate" handsheets provides porosity to the paper, gives shorter drainage times in the handsheet making process, and enhances the ash characteristics of cigarettes prepared from these papers. Sidestream smoke data of cigarettes prepared with papers containing "mag carbonates" and different calcium carbonate co-fillers show differences in visibility reduction. Evaluations of other calcium carbonate co-fillers are being conducted to determine if there are advantages in using one calcium carbonate sample over another.

Reevaluation of several "mag carbonate" samples synthesized earlier in the year have shown the samples to have undergone an aging process, i.e. a change in crystallinity. Work is being conducted to better understand this process and how it might effect the smoking properties of a given material.

Studies are being conducted to better understanding the nature of the soluble magnesium bicarbonate species believed to be the intermediate to solid "mag carbonate" phases. In one study, the reaction, in water, of magnesium hydroxide with carbon 13 labelled carbon dioxide was conducted, and the resulting solution was examined by ^{13}C NMR. Initial results indicate that the reaction proceeds slowly. ^{13}C NMR shows only one peak at ~165 ppm. Identification of the chemical species giving rise to this signal will require additional standards. The solid material filtered from this reaction is also in the process of being characterized. In another study the ratio of carbon dioxide to the dissolved magnesium (crucial for developing reproducibility in the above chemistry) is being examined using a gravimetric technique. A plot of carbon dioxide content versus pH at constant magnesium content is the ultimate goal of the latter study.

In the interest of comparing the mainstream smoke chemistry of low sidestream cigarettes sized with hexapotassium phytate versus those sized with conventional fluxing agents, cigarettes have been prepared from E2560 $CaCO_3$ papers sized with either K_6 phytate or K_2 succinate. The cigarettes have been submitted to Analytical Research for the requisite analyses.

A series of intermediate basis weight papers containing different levels of $CaCO_3$ at different porosities were sized with tripotassium and hexapotassium phytate. At low levels of application the tripotassium salt increased the porosity of the papers substantially and had no effect on the sidestream smoke level of cigarettes made from these papers. At slightly higher levels of application the hexapotassium phytate showed no effect on paper porosity and exhibited a modest level of sidestream reduction with acceptable static burn times. Further evaluations of these materials in sizing applications are planned.

Hexapotassium phytate solutions at 26% and 50% solids have been used to coat bands onto standard cigarette papers via the gravure process. The strips of paper having band-coatings of 7mm wide have been used to prepare machine made cigarettes. These samples have been submitted to Physical Research for evaluation of mass burn-rate as well as other routine analyses.

During the month, we have reviewed proposals to Philip Morris as well as to the Virginia Center for Innovative Technology from Dr. Richard Zallen of Virginia Tech. A response to Dr. Zallen will be prepared after we assess completely the impact of his proposals to PM interests. We have also reviewed and discussed a preliminary proposal for 1991 from Dr. Donald Schleich of N.Y. Polytechnic University. This proposal should be finalized shortly.

II. REMOVAL OF NICOTINE FROM AQUEOUS TOBACCO PROCESSING FLUIDS
(Howe)

A. **Objective:** To develop techniques to remove selectively nicotine and other alkaloids from aqueous tobacco processing fluids.

B. **Results and Plans:** Old samples of MPC solution from water column runs at the BHPP have been discarded. One of the solutions form April of this year was reanalyzed for nicotine concentration at the request of D. Teng as a comparison to the original analysis done in April at the BHPP. No change in the nicotine concentration was noticed even though the sample was darker in color and smelled "degraded" or "fermented".

III. MISCELLANEOUS
(Secor)

One of a series of nicotinoids for R. Carchman has been prepared and work continues on the preparation of others.

2022201528

Structures of Substrates

calcium carbonate, calcite [$CaCO_3$]

eitelite [$Na_2Mg(CO_3)_2$]

hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$]

magnesium hydroxide, brucite [$Mg(OH)_2$]

magnesite [$MgCO_3$]

nesquehonite [$MgCO_3 \bullet 3H_2O$]

phytate = myo-inositolhexaphosphate